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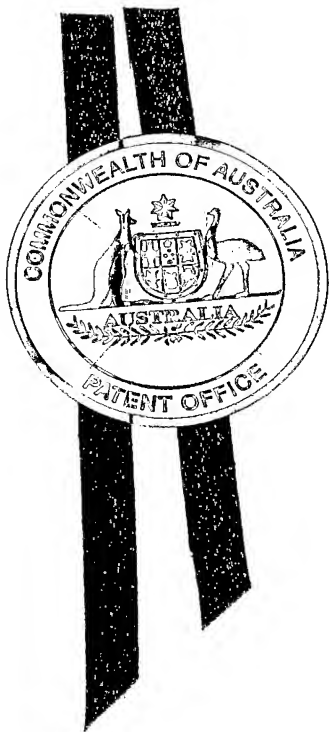
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I, JANENE PEISKER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2004900457 for a patent by COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION as filed on 28 January 2004.

WITNESS my hand this  
Eighth day of February 2005

A handwritten signature in cursive script, appearing to read 'J. Peisker'.

JANENE PEISKER  
TEAM LEADER EXAMINATION  
SUPPORT AND SALES



AUSTRALIA  
Patents Act 1990

**PROVISIONAL SPECIFICATION**

**Applicant:**

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH  
ORGANISATION

**Invention Title:**

A NOVEL PROCESS TO RECOVER NICKEL AND COBALT FROM  
AQUEOUS SOLUTIONS BY SYNERGISTIC SOLVENT EXTRACTION

The invention is described in the following statement:

A SOLVENT EXTRACTION PROCESS FOR SEPARATING NICKEL AND/OR  
COBALT FROM IMPURITIES IN LEACH SOLUTIONS.

5 The present invention relates to a process for separating  
cobalt and/or nickel from other elements contained in an  
aqueous solution such as an aqueous leach solution, and  
for recovering the cobalt and/or nickel where desired.

10 The world mineral industry is experiencing an  
unprecedented interest in nickel-cobalt extraction from  
laterite ores through pressure acid leach (PAL) and  
solvent extraction - electrowinning (SX-EW) processes. In  
Western Australia, three nickel laterite plants are in  
operation. These are the Cawse, Bulong and Murrin Murrin  
15 nickel plants. In New Caledonia, the Goro process has been  
tested in a large pilot plant. The PAL process for these  
projects is very similar, however the down stream  
processes (especially SX) differ substantially.

20 In the Murrin Murrin process, a sulphide precipitation is  
used to separate the nickel, cobalt, copper and zinc from  
impurities such as calcium, magnesium and manganese, which  
remain in the leach solution. After solids/liquid  
separation, the nickel, cobalt, copper and zinc are re-  
25 leached under pressure with acid. Further solution  
purification is needed to separate nickel and cobalt from  
copper and zinc. The cobalt is then separated from nickel  
by solvent extraction with Cyanex 272. The nickel and  
cobalt are recovered by reduction with hydrogen. The  
30 drawbacks of the Murrin Murrin process are:

- The separation of manganese from cobalt by sulphide  
precipitation is incomplete and causes problems in the  
downstream processes,
- The leaching of sulphides needs high pressure and high  
35 temperature, indicating high capital and operating  
costs.

- The separation of other impurities such as copper and zinc from nickel and cobalt needs separate processes.

5 In the Cawse process, a hydroxide precipitation is used to  
separate the impurities such as calcium, magnesium and  
manganese (partly). After solids/liquid separation, the  
nickel, cobalt, copper, zinc and some manganese are re-  
leached with an ammoniacal solution. Nickel and copper are  
10 separated from cobalt and zinc by solvent extraction with  
LIX84I. Further solution purification is needed to  
separate nickel from copper and cobalt from zinc. The  
nickel is recovered by electrowinning while cobalt is  
precipitated as sulphide. The drawbacks of the Cawse  
process are:

- 15 • The use of magnesia as precipitation agent adds cost to operation,
- The use of ammoniacal leaching to separate manganese from nickel and cobalt results in complexity of the flowsheet and causes serious problems in the downstream  
20 processes,
- The reductive stripping of cobalt from organic extractant and the re-oximation of the organic extractant cause organic degradation, which in turn results in crud formation,
- 25 • Ammonia is expensive and the scrubbing and recovery of ammonia are difficult,
- Cobalt product containing zinc is a semi-product, indicating revenue loss.

30 The Bulong process uses a direct solvent extraction approach. Cobalt, copper, zinc and manganese are separated from nickel, calcium and magnesium by solvent extraction with Cyanex 272. The nickel in the raffinate is separated from calcium and magnesium by solvent extraction with  
35 Versatic 10 and then electrowon. The solution containing cobalt, copper, zinc and manganese is subjected to sulphide precipitation, solids/liquid separation and acid

pressure re-leach to separate cobalt, copper and zinc from manganese. The copper is eliminated from the solution by ion exchange and zinc by solvent extraction with D2EHPA. The cobalt is then recovered from the purified solution by electrowinning. The drawbacks of the Bulong process are:

- Manganese is separated from cobalt by sulphide precipitation and other impurities are separated by different further processes (ion exchange and further SX),
- Gypsum precipitation occurs in both Cyanex 272 and Versatic 10 circuits,

Other processes have been developed to varying extents for the direct solvent extraction of nickel and cobalt, including the Goro process. Such processes suffer from varying disadvantages, including:

- the need to remove copper from the leach solution before it enters the extraction circuit, thus requiring a large volume of the leach solution to pass through two circuits,
- the requirement for high acidity (6M HCl), high temperature (60°C) and longer than usual stripping time (5 minutes) to strip the nickel, cobalt and zinc from the loaded organic solution,
- high cost in recovering and recycling the expensive HCl and further difficulties associated with corrosiveness of the acid, and
- the need to regenerate the organic extractant due to degradation of the extractant in the process.

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Other processes can suffer from difficulties in phase separation and lack of availability of extractants or other agents required for the process.

35 It is an object of the invention to provide an alternative process for separating nickel and/or cobalt from other

elements that avoids some of the disadvantages of the existing methods.

Summary of the Invention

5 According to the present invention there is provided a process for the separation of nickel, cobalt or both from impurity elements contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using a carboxylic acid and  
10 a hydroxyoxime.

The solvent extraction step described above achieves very good separation of nickel and cobalt present in the leach solution from calcium, magnesium, manganese and chloride  
15 impurity elements which may be present. Greater process efficiencies can be obtained according to a preferred embodiment of the invention, wherein the solvent extraction step with carboxylic acid and hydroxyoxime is conducted in the presence of a kinetic accelerator. The  
20 kinetic accelerator, such as tributyl phosphate (TBP), is capable of enhancing the stripping and extraction kinetics and thus enhances the commercial advantages of the invention.

25 According to a preferred embodiment, the nickel, cobalt or both extracted into the organic phase during the solvent extraction are recovered from the organic phase. As explained in the detailed description below, the nickel and cobalt are separated from each other and recovered  
30 separately in the subsequent treatment stages.

According to one embodiment, the recovery step comprises selective stripping of the organic phase to separate the cobalt from the nickel. The cobalt may thereafter be  
35 recovered from the loaded aqueous strip liquor, and the nickel recovered from the selectively stripped organic solution by bulk stripping.

Brief Description of the Drawings

5 The invention will be described in further detail with reference to the following figures which relate to preferred embodiments of the invention.

10 Figure 1 is a schematic flow chart of the steps of the process of one embodiment of the invention.

Figure 2 is a more detailed schematic flow chart of a part of the process illustrated in Figure 1.

15 Figure 3 is a schematic flow chart of a second embodiment of the invention, which is a variation on the process illustrated in Figure 2.

20 Figures 4 and 5 are graphs comparing extraction pH isotherms of metals using a comparative extraction system (Figure 4) and the extraction system of one embodiment of the invention (Figure 5).

25 Figure 6 is a graph showing the stripping kinetics of metals from a loaded organic phase from the extraction system of a second embodiment of the invention.

Figure 7 is a graph showing the Extraction pH isotherms of metals from the organic phase of system of Figure 6.

30 Figure 8 is a graph showing the extraction kinetics of metals from the organic phase of system of Figure 6.

35 Figure 9 is a graph showing the stripping pH isotherms of metals from the organic phase of the system of Figure 6.

Figure 10 is a detailed schematic flow chart of a third embodiment of the invention.



### Detailed Description of the Invention

5 At the core of the present invention is a synergistic solvent extraction step which effects extraction of a large proportion of the nickel, cobalt, copper and zinc into an organic phase (to the extent that these elements are present), with a large proportion of the calcium, magnesium, manganese and chloride being rejected to the  
10 aqueous phase. The solvent extraction is conducted with a combination of carboxylic acid and a hydroxyoxime synergist, and according to a preferred embodiment, with a kinetic accelerator.

15 The hydroxyoxime synergist is capable of increasing the pH gap,  $\Delta\text{pH}_{50}$ , between isotherms for nickel and cobalt and those for manganese, calcium and magnesium. This results in advantageous selectivity of nickel and cobalt over the  
20 impurities manganese, calcium, magnesium and chloride.

The  $\text{pH}_{50}$  value is the pH at which 50% metal extraction is achieved. Thus,  $\Delta\text{pH}_{50}$  is the difference between the  $\text{pH}_{50}$  values for two metals.

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#### Carboxylic acid

In the most preferred embodiment of the invention, the carboxylic acid is 2-hexyl, 2-methyl octacarboxylic acid (commercially available as Versatic 10) or a cationic  
30 exchange extractant having extraction characteristics similar to 2-hexyl, 2-methyl octacarboxylic acid could be used. Cationic exchange extractants have hydrogen ions which are exchanged with metal ions in the aqueous solution. The term carboxylic acid is used in its broadest  
35 sense to refer to any organic carboxylic acid. Carboxylic acids have the formula  $\text{RCOOH}$ , in which R represents any optionally substituted aliphatic or aromatic group, or

combinations of these groups, including optionally substituted alkyl, alkenyl, alkynyl, aryl, or heteroaryl groups (and combinations thereof). Preferably R represents a relatively bulky group containing at least 4 carbon atoms, and preferably between 4 to 18 carbon atoms.

The term "alkyl" used either alone or in a compound word such as "optionally substituted alkyl" or "optionally substituted cycloalkyl" denotes straight chain branched or mono- or poly-cyclic alkyl, preferably C1-30 alkyl or cycloalkyl, most preferably C4-18 alkyl. Examples of straight chain and branched alkyl include methyl, ethyl, butyl, isobutyl, tert-butyl, 1,2-dimethylpropyl, 1-methylpentyl, 5-methylhexyl, 4,4-dimethylpentyl 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,1,2-trimethylbutyl, nonyl, 1- 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 2-hexyl 2-methyloctyl and the like. Examples of cyclic alkyl include cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclodecyl and the like. The alkyl may optionally be substituted by any non-deleterious substituent.

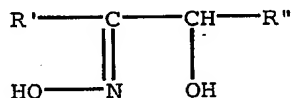
In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl,

alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthiom benzylthio, acylthio and the like.

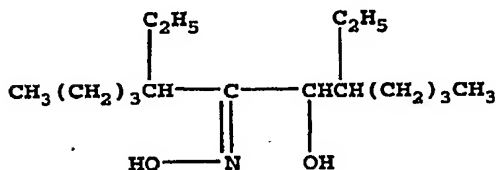
Suitable optional substituents will be chosen on the basis that the carboxylic acid have the desired extraction characteristics, and the substituents do not react with any other component of the mixture under the given extraction conditions.

#### 10 Hydroxyoxime

A hydroxyoxime is used as a synergist with the carboxylic acid in the solvent extraction step. A hydroxyoxime is a compound containing an oxime group and a hydroxy group. Preferably, the groups are in an  $\alpha$ -position with respect to each other. The "oxime" functional group contains a carbon to nitrogen double bond, with the nitrogen atom being attached to an oxygen atom. Accordingly, the term oxime includes within its scope oximes with a hydroxy group attached to the nitrogen atom, and oxime ethers, although hydroxime ( $>C=N-OH$ ) is preferred. The hydroxyoxime may be a C6-C26 hydroxyoxime. Preferably, the hydroxyoxime is an aliphatic hydroxyoxime. Preferably, the hydroxyoxime is of the formula:



25 in which R' and R'' are each selected from an optionally substituted, straight chain, branched or cyclic alkyl, group containing from 2 to 12 carbon atoms. Preferably each of R' and R'' are unsubstituted alkyl groups, most preferably a heptyl group. An example of such a compound is 5,8-diethyl-7-hydroxy-6-dodecanone oxime (the active component of a commercial agent LIX 63). This has the following structure:



#### Kinetic accelerator

A kinetic accelerator is an agent that improves the  
5 extraction and/or stripping kinetics of metals. Examples  
of kinetic accelerators in this class are tri n-butyl  
phosphate (TBP), 2-ethylhexanol, isodecanol, isotridecanol  
and nonyl phenol. Any reagent that performs the function  
of increasing the rate of extraction and stripping may be  
10 used the kinetic accelerator for the purpose of this  
invention. TBP is the preferred kinetic accelerator in  
the current invention.

#### Leach solution

15 The leach solution subjected to the synergistic solvent  
extraction with carboxylic acid and hydroxyoxime may be  
any type of leach solution containing nickel and/or  
cobalt, together with impurity elements selected from one  
or more of calcium, magnesium, manganese and chloride,  
20 optionally together with copper and zinc. Preferably, the  
leach solution is one containing each of these impurity  
elements. The leach solution may for instance be a  
pregnant leach solution obtained from the pressure acid  
leaching of any suitable ore type, such as a laterite or  
25 sulphide ore. It may alternatively be a solution from bio-  
leach, atmospheric acid leach, oxidative leach or chloride  
leach processes. The steps involved in producing such  
leach solutions are well known in the art.

30 The leach solution may be a solution that has been  
subjected to a preliminary iron precipitation step to  
precipitate out iron to leave an aqueous leach solution

containing the target elements and impurity elements identified above.

Synergistic solvent extraction conditions

5 The solvent extraction step involves contacting an organic solvent containing the carboxylic acid and hydroxyoxime with the (aqueous) leach solution. The organic solvent may be any suitable organic solvent known in the art. Kerosene is the most common solvent/diluent used for this purpose due to its low cost and availability. Shellsol 10 2046 is one specific example.

The amount of carboxylic acid and hydroxyoxime in the organic solution used in the solvent extraction step will 15 depend on the concentration of the nickel, cobalt or both to be extracted and the A/O (aqueous/organic) flow rate ratio. The concentration would typically be in the range of from 0.1 to 2.0 M for carboxylic acid, with a preferred range of 0.1 to 1.0M, and 0.05 to 1.0 M for hydroxyoxime.

20 The amount of kinetic accelerator in the organic solution used in the extraction step will also vary. The range of kinetic accelerator will typically be in the range of 0.1 to 5 M, with a preferred range of 0.1 to 1.0 M.

25 Preferably, the pH of the aqueous phase is maintained in a range from 5.0 to 6.5 and more preferably 5.5 to 6.0 in the extraction step. The temperature is preferably maintained in the range of from 10°C to 60°C, more 30 preferably from 20 to 40°C. Whilst temperatures as low as 10°C are achievable, a temperature lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of evaporation and degradation of the organic phase.

35 The aqueous to organic ratio (A/O) in the extraction step is most preferably 1:1, but may lie in the range from 10:1

to 1:10, and preferably 1:5 to 5:1. The aqueous to organic ratio maintained in the scrubbing step may lie within the range of from 1:5 to 1:200, but preferably it is in the range of 1:5 to 1:20.

5

The nickel and/or cobalt extracted into the loaded organic phase in the synergistic solvent extraction is recovered in downstream processing stages.

10 Scrubbing

The organic phase from the synergistic extraction step of the invention is suitably subjected to scrubbing. The scrub solution may suitably be a process stream recycled from the process, and is preferably derived from an aqueous stream of a stripping stage (which may be a selective stripping stage) following the scrubbing stage. The scrub solution suitably contains cobalt and zinc sulphate, optionally with some nickel and copper.

20 Recovery of nickel, cobalt or both from scrubbed organic solution

There are a number of options envisaged by the applicants for the recovery of nickel, cobalt or both from the scrubbed organic solution. Two options having particular advantages in combination with the synergistic solvent extraction stage of the invention are described below. Nevertheless, it is noted that other options within the skill and knowledge of those in the art could be used in place of the following, and are within the scope of the present invention.

30

Option 1: Selective stripping

According to one embodiment of the invention, the organic phase is subjected to selective stripping to separate to a significant extent the nickel and the cobalt. The selective strip suitably involves contacting the organic phase from the synergistic extraction with an acidic

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- aqueous solution to yield (a) a loaded strip liquor containing cobalt (and zinc, if this was present in the organic phase from the synergistic extraction), and only a small amount of nickel (and possibly copper), and (b) a
- 5 selectively stripped organic solution containing nickel (and copper, if this was present in the organic phase from the synergistic extraction) and only a small amount of cobalt (and possibly zinc).
- 10 The acidic aqueous solution for the selective strip is suitably sulphuric acid solution, although other aqueous acid solutions known in the art (such as hydrochloric) may be used. The pH of the acidic aqueous solution is
- 15 suitably in the range of about 3.0 to 4.0, depending on the level of separation desired. Most preferably, the pH is about 3.5.

The combination of the described synergistic extraction with the selective strip of cobalt from nickel is a very

20 useful combination, enabling the recovery of nickel and cobalt using only one solvent extraction circuit (although more than one circuit could be used if so desired with other process steps). Thus, according to one embodiment of the invention, the process comprises a single solvent

25 extraction circuit.

*Recovery of nickel, cobalt or both following selective stripping*

Various options are envisaged for the recovery of nickel,

30 cobalt or both following the selective stripping.

*Cobalt*

The loaded strip liquor containing cobalt (and possibly zinc) may be subjected to cobalt precipitation using a

35 base or sulphide. The product of this step is a mixed hydroxide product (MHP) or mixed sulphide product (MSP). Cobalt precipitation is a known and commercially used

process step in the minerals industry, and therefore the details of this step require no further discussion here.

Alternatively, the loaded strip liquor may be recovered as  
5 pure cobalt products, optionally preceded by copper/zinc and/or nickel ion exchange.

#### *Nickel*

The stripped organic solution from the selective stripping  
10 step contains nickel (and possibly copper). If copper is present, nickel is separated from the copper using any suitable process known in the art. The following is a description of one preferred series of steps for recovering the nickel.

15 The organic solution from the selective stripping step (which is optionally scrubbed) is subjected to stripping with an aqueous acid solution of a suitable pH to separate the nickel into the aqueous phase with only a small amount  
20 of the copper. This loaded strip liquor may then be subjected to ion exchange to remove copper, with the nickel reporting to the raffinate. The raffinate containing nickel with minimal impurities may then be recovered by any suitable process such as electrowinning.  
25 Details of the ion exchange and electrowinning stages are well known in the art of the invention.

Process streams from the above stages are suitably recycled to minimise loss of valuable elements and  
30 maximise process efficiency. The optional scrubbing of the organic solution from the selective stripping stage suitably involves the use of the nickel (and copper) containing aqueous solution (eg sulphate solution) from the subsequent stripping stage. The stripping of nickel  
35 from the organic solution may be conducted with the nickel spent electrolyte from the nickel electrowinning step, which contains acid (typically sulphuric acid) and a



relatively low concentration of nickel. Then the stripped organic solution containing small amounts nickel (and copper) from this second stage of stripping may be recycled to the selective extraction stage to minimise loss of nickel. Finally, the nickel spent electrolyte can be recycled to the nickel stripping stage.

Recovery of nickel and cobalt from purified leach solutions by electrowinning, precipitation or any other appropriate process, is best performed after the metals have been concentrated to an appropriate level (often of the order of 60g/L). The process described above is suitable for concentrating the nickel and cobalt to these levels. This compares with the typical concentrations an originating leach solutions, such as a laterite leach solution, of around 1.0 - 4.0g/L nickel and 0.1 - 0.4g/L cobalt.

Option 2: Second SX circuit with organophosphinic acid

After scrubbing, the scrubbed organic solution can be completely stripped to obtain (a) a loaded strip liquor containing nickel and cobalt (and copper and zinc impurities), and (b) a stripped organic solution.

The loaded strip liquor thus obtained can be subjected to organophosphinic acid solvent extraction, using a suitable organophosphinic acid such as Cyanex 272. This extraction stage, and the identity of organophosphinic acids, are as described in co-pending application PCT/AU01/01161, the full disclosure of which is incorporated herein by reference.

In the case of the use of Cyanex 272, the loaded organic solution from the Cyanex extraction step contains cobalt (and zinc and copper, to the extent they are present) and only a small amount of nickel. The loaded Cyanex organic solution is scrubbed, and the scrubbed organic solution

containing cobalt (copper and zinc) is subjected to stripping with diluted sulphuric acid of an appropriate pH. The loaded strip liquor containing cobalt (copper and zinc) is subjected to ion exchange to remove copper and zinc present. The raffinate containing only cobalt can then be subjected to electrowinning, hydrogen reduction or precipitation, as desired, to recover the cobalt.

The aqueous raffinate from the Cyanex extraction stage containing nickel may be subjected to electrowinning, hydrogen reduction or precipitation to recover the nickel therefrom.

Details of preferred features regarding this option, and particularly the recycling of process streams, will be explained below with reference to the figures.

#### Other process details

The synergistic extraction step of the present invention may be combined with different preliminary and following process steps for the development of processes suitable for the recovery of cobalt and/or nickel when different impurity elements may be present.

It will be well understood to persons skilled in the art of the invention that scrubbing stages of the type well known in the art may be used for recovering elements even if the scrubbing stages are not specifically mentioned. The design of the optimum arrangement of scrubbing stages will depend on the specific aqueous leach solution and the elements desired to be recovered therefrom (and target percentage recovery levels).

It is also an advantage of the present invention that cobalt and/or nickel can be separated from impurities contained in leach solutions without intermediate

precipitation of the cobalt and/or nickel with other impurity elements and re-leaching of the precipitate to subsequently enable the removal of the impurities. Thus, in a preferred embodiment of the invention, the process does not include a precipitation step involving precipitation out of the target elements and re-leaching of the precipitate.

#### Examples

The present invention will now be described in further detail with reference to the following examples and process flowcharts, which demonstrate the underlying theory behind the invention, and how the invention is put into practice.

#### *Batch Test Work*

Example 1 - Extraction pH isotherms of metals with Versatic 10 / LIX63 synergistic system.

The aqueous solution was a synthetic solution to simulate a typical laterite leach solution containing 3 g/L Ni, 0.3 g/L Co, 0.2 g/L Cu and Zn, 2 g/L Mn, 10 g/L Mg and 0.5 g/L Ca.

The metal extraction pH isotherms with the 0.5 M Versatic 10 (carboxylic acid) alone were determined and plotted, as shown in Fig. 4. The metal extraction pH isotherms using the combination of 0.5 M Versatic 10 and 0.35 M LIX63 (hydroxyoxime) were also determined and plotted in Figure 5. Comparison of the two figures reveals that the combination of LIX63 with Versatic 10 resulted in significant synergistic extraction isotherm shifts (to lower pH) for nickel, cobalt, copper, zinc, and manganese and antagonistic shifts (to higher pH) for calcium and magnesium. As shown in Figure 5, with the 0.5 M Versatic 10 / 0.35 LIX63 system, the  $\Delta\text{pH}_{50}$  values of nickel, cobalt, copper, zinc, and manganese were found to be 2.79, 3.50, >3.0, 1.99 and 1.17 pH units, respectively. The  $\Delta\text{pH}_{50(\text{Mn-Ni})}$  value for the 0.5 M Versatic 10 / 0.35 M LIX63 system was

found to be 1.96 pH units and the  $\Delta\text{pH}_{50(\text{Mn-Co})}$  value 2.53 pH units, indicating easy separation of nickel and cobalt from manganese, calcium and magnesium.

5 Example 2 - Extraction kinetics with Versatic 10 / LIX63 synergistic system.

Tests were conducted to establish the extraction kinetics of the metals in the synthetic laterite solution using Versatic 10/LIX63. The extraction kinetics of copper,  
10 cobalt and zinc and manganese were found to be fast and the extraction kinetics of nickel were found to be relatively slow. Within 30 seconds, only 54.6% Ni was extracted within 10 minutes 85.5%.

15 Example 3 - Stripping kinetics with Versatic 10 / LIX63 synergistic system.

Tests were conducted to determine the stripping kinetics of the metals from the 0.5 M Versatic 10 / 0.35 M LIX63 system. The stripping kinetics of copper, cobalt and zinc  
20 were fast. The stripping kinetics of nickel were slow, with 17.7% Ni stripped in 2 minutes and 31.8% in 5 minutes. Improvements in the stripping kinetics are demonstrated below when the kinetic accelerator TBP is used in combination with the carboxylic acid and  
25 hydroxyoxime.

Example 4 - Stripping of cobalt from LIX63 alone and Versatic 10 / LIX63 systems.

Cobalt(II) can poison hydroxyoxime reagents such as  
30 LIX63.. This means that once cobalt(II) is extracted by hydroxyoxime reagents, it cannot be stripped with concentrated acids. Tests were conducted to see whether the new system results in cobalt poisoning.

35 Parallel tests were conducted with 0.35 M LIX63 alone and 0.5 M Versatic 10 / 0.35 M LIX63 systems by mixing the organic solutions with aqueous solution containing cobalt.

The organic and aqueous solutions were left in contact with air bubbling for 76 hours. Thereafter, a sulphuric acid solution of 100 g/l sulphuric acid was used to strip cobalt from the organic solution. The cobalt stripping efficiency from the 0.35 M LIX63 alone system was only 29.2%. The cobalt stripping efficiency for the 0.5 M Versatic 10 / 0.35 M LIX63 system was 99.5%. This indicates that cobalt(II) does not poison the Versatic 10 / LIX63 system.

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Example 5 - Stripping kinetics with Versatic 10 / LIX63 / kinetic accelerator system.

Example 3 was repeated with the 0.5 M Versatic 10, 0.35 M LIX63 and 0.5M TBP system. In 2 minutes, whereas Example 3 resulted in stripping of only 17.7% of nickel, this increased to 91.3% when the extractant system included a kinetic accelerator TBP. Moreover, as demonstrated in Example 6, the addition of TBP to the Versatic 10 / LIX63 system had no adverse effect on the selectivity of nickel and cobalt over manganese. The tests were repeated using isotridecanol as the kinetic accelerator, and similar results were achieved.

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Example 6 - Extraction pH isotherms with Versatic 10 / LIX63 / kinetic accelerator system.

The extraction pH isotherms were determined for the Versatic 10 / LIX63 / TBP system and these are shown in Figure 7. The addition of TBP to the Versatic 10 / LIX63 system resulted in large antagonistic shifts for Ni, Co, Zn and Mn. The  $\Delta\text{pH}_{50}$  shifts for Ni, Co, Zn and Mn were -0.63, -1.71, -1.35 and -1.28, respectively. However, the  $\Delta\text{pH}_{50(\text{Mn-Ni})}$  and  $\Delta\text{pH}_{50(\text{Mn-Co})}$  values were still greater than 2 pH units. This indicates that the addition of TBP to the Versatic 10 / LIX63 system had no adverse effect on the selectivity of nickel and cobalt over manganese. In addition, the cobalt pH isotherm was shifted at the right of nickel, making the selective stripping of cobalt

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practical.

Example 7 - Extraction kinetics with Versatic 10 / LIX63 / kinetic accelerator system.

5 The extraction kinetics of the metals in the synthetic laterite leach solution using the 0.5 M Versatic 10 / 0.35 M LIX63 / 0.5 M TBP system were determined and graphed in Figure 8. As shown, the extraction kinetics of Ni, Co, Cu, Zn and Mn were fast. Within 2 minutes, the nickel  
10 extraction reached 95.2%, which was fast enough for industrial operations.

Example 8 - Stripping pH isotherms.

Tests were conducted to determine the pH required to strip  
15 the metals from the loaded organic systems, and the results are demonstrated in Figure 9. At pH 3.50, more than 94% Co and only 3.6% Ni could be stripped, indicating that cobalt can be separated from nickel by selective stripping. Therefore, it was determined that only one SX  
20 circuit is required to separate nickel and cobalt from Mn, Ca and Mg and also to separate nickel and cobalt from each other.

#### *Process Flowcharts*

25 Example 9 - Process for separation and recovery of cobalt and nickel from leach solution.

Based on the above findings, a new DSX process flowsheet was formulated. The flowsheet is shown in Figures 1 and 2. By using the Versatic 10 / LIX63 synergistic system, a  
30 kinetic accelerator TBP and a selective stripping strategy, three goals are achieved in one SX circuit: the separation of nickel and cobalt from manganese, magnesium, calcium and chloride, the separation of cobalt from nickel and the concentration of cobalt and nickel.

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PAL

As shown in Figure 1, a nickel and cobalt containing ore,

such as a laterite ore, is subjected to pressure acid leaching in accordance with standard procedures known in the art.

5    Neutralisation

The leach solution is subjected to neutralisation with limestone at pH 4.5 - 5.0 to precipitate impurity elements Fe(III), Al, Si and Cr.

10   Synergistic solvent extraction (EX)

The synergistic solvent extraction and following stages are represented briefly in Figure 1, and are expanded upon in Figure 2. The pregnant leach solution (PLS) from the neutralisation or iron precipitation step is subjected to the synergistic solvent extraction (SX) step. In this step an organic solution of a carboxylic acid (Versatic 10 acid) and a hydroxyoxime (5,8-diethyl-7-hydroxy-6-dodecanone oxime - (LIX63)), and a kinetic accelerator, tributyl phosphate (TBP), in organic diluent ShellSol 2046 is contacted with the PLS to obtain (a) an aqueous raffinate containing almost all the manganese, magnesium, calcium and chloride and (b) a loaded organic solution containing almost all the nickel, cobalt, copper, zinc and very small amount of manganese.

25

Scrubbing (SC1)

The organic solution from the extraction step is subjected to scrubbing 1 using a cobalt and zinc sulphate solution containing a small amount of nickel and copper from the next step stripping 1, resulting in (a) a scrubbed organic solution containing nickel, copper, cobalt and zinc and (b) a loaded scrub liquor containing mainly manganese, and small amounts of cobalt, zinc nickel and copper, which is recycled to the extraction step.

35

Selective stripping (ST1)

The scrubbed organic solution is subjected to stripping 1

(selective strip) using a sulphuric acid solution, resulting in (a) a loaded strip liquor containing cobalt and zinc and small amount of nickel and copper and (b) a stripped organic solution containing mainly nickel and copper and a very small amount of cobalt and zinc.

#### Scrubbing (SC2)

The organic solution from stripping 1 is subjected to scrubbing 2 using a nickel and copper sulphate solution from the next step stripping 2, resulting in (a) a scrubbed organic solution containing nickel and copper and (b) a loaded scrub liquor containing cobalt, zinc and some nickel and copper which is recycled to the extraction step.

#### Stripping (ST2)

The scrubbed organic solution is subjected to stripping 2 using a nickel spent electrolyte from the nickel electrowinning step containing sulphuric acid and a relatively low concentration of nickel, resulting in (a) a loaded strip liquor containing a high concentration of nickel and a small amount of copper and (b) a stripped organic solution containing a very small amount of nickel and copper, which is recycled to the extraction step.

#### Ion Exchange (IX) and Electrowinning (EW)

The loaded strip liquor from stripping 2 is subjected to an ion exchange step to remove copper and the raffinate from the ion exchange step is subjected to nickel electrowinning, resulting in a high-grade nickel metal product. The copper ion exchange and nickel electrowinning are known processes and commercially used in the minerals industry.

#### Cobalt precipitation (PPT)

The loaded strip liquor from stripping 1 is subjected to cobalt precipitation using base or sulphide, resulting in sellable products mixed hydroxide product (MHP) or mixed



sulphide product (MSH). The cobalt precipitation is a known process and commercially used in the minerals industry.

5 Example 10 - Variation on Process of Example 9

Pure cobalt products can be obtained from the loaded liquor from strip 1 using ion exchange to remove copper, zinc and nickel. The details of the steps are shown in Figure 3.

10

The loaded strip liquor from stripping 1 (selective strip) in the SX circuit is subjected to an ion exchange step, resulting in (a) a raffinate liquor containing cobalt and a small amount of nickel, and (b) a waste solution  
15 containing copper and zinc for disposal. This is a known process and commercially used in the minerals industry. The raffinate liquor is subjected to another ion exchange step, resulting in (a) a desorption solution containing nickel and a small amount of cobalt, which is recycled to  
20 the extraction step, and (b) a pure cobalt solution to a cobalt recovery step, where cobalt cathodes can be obtained by electrowinning or a variety of cobalt chemical products by precipitation as required. These are known processes and commercially used in the minerals industry.

25

Example 11 - Second variation on the Process of Example 9

According to this variation, a second solvent extraction circuit is used to separate nickel and cobalt with Cyanex 272 in a diluent such as Shellsol 2046. This process is  
30 represented in a flowchart in Figure 9.

After scrubbing, the scrubbed organic is subjected to a stripping step using the spent electrolyte from nickel electrowinning step to obtain (a) a loaded strip liquor  
35 containing nickel, cobalt, copper and zinc and (b) a stripped organic solution which is recycled to extraction step.

The loaded strip liquor is subjected to an extraction step using Cyanex 272 to obtain (a) a raffinate solution containing only nickel and (b) a loaded organic solution  
5 containing cobalt, zinc, copper and small amount of nickel.

The loaded Cyanex 272 organic solution is subjected to scrubbing with a scrub solution from the next stripping  
10 step, resulting in (a) a loaded scrub liquor containing nickel and some cobalt, zinc and copper which is recycled to the extraction step, and (b) a scrubbed organic solution containing cobalt, copper and zinc.

15 The scrubbed Cyanex 272 organic solution is subjected to a stripping step with diluted sulphuric acid, resulting in a loaded strip liquor containing cobalt, zinc and copper, and a stripped organic solution which is recycled for extraction.

20 The loaded strip liquor is subjected to an ion exchange step to remove copper and zinc, resulting in (a) a raffinate solution containing only cobalt and a waste solution containing copper and zinc for disposal.

25 The pure cobalt sulphate solution could be subjected to (a) electrowinning to obtain cobalt cathodes, and (b) precipitation with a base to obtain cobalt hydroxide, or with hydrogen sulphide to obtain cobalt sulphide, or with  
30 a carbonate solution to obtain cobalt carbonate.

It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

35

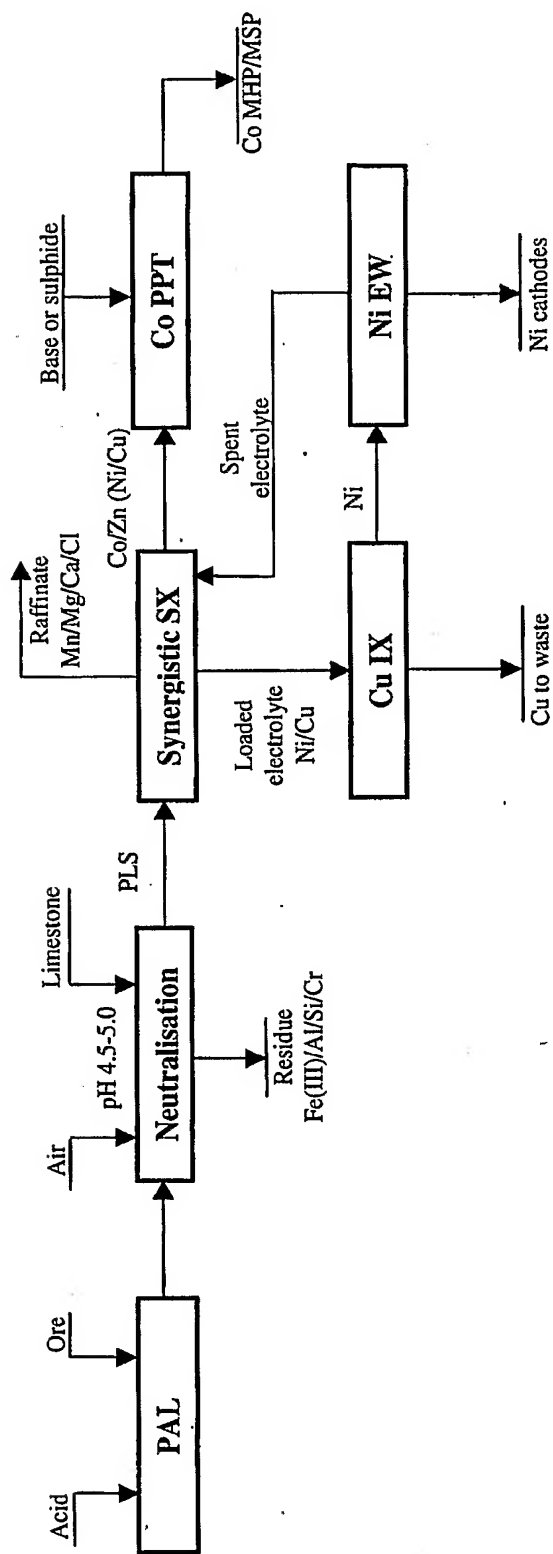
Dated this 28th day of January 2004

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH  
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By their Patent Attorneys

5 GRIFFITH HACK

Fellows Institute of Patent and  
Trade Mark Attorneys of Australia



1. Minor elements in brackets

Figure 1

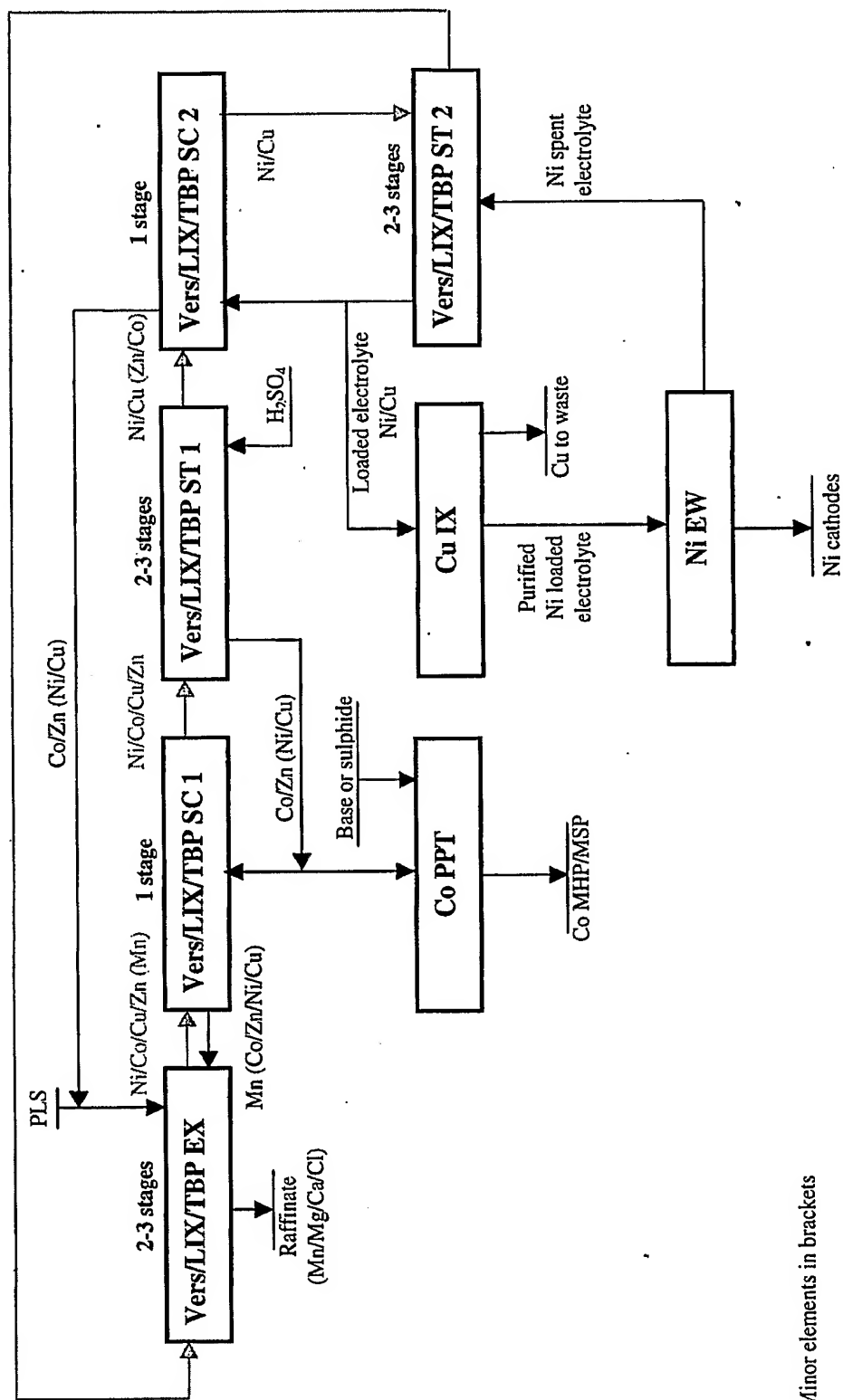
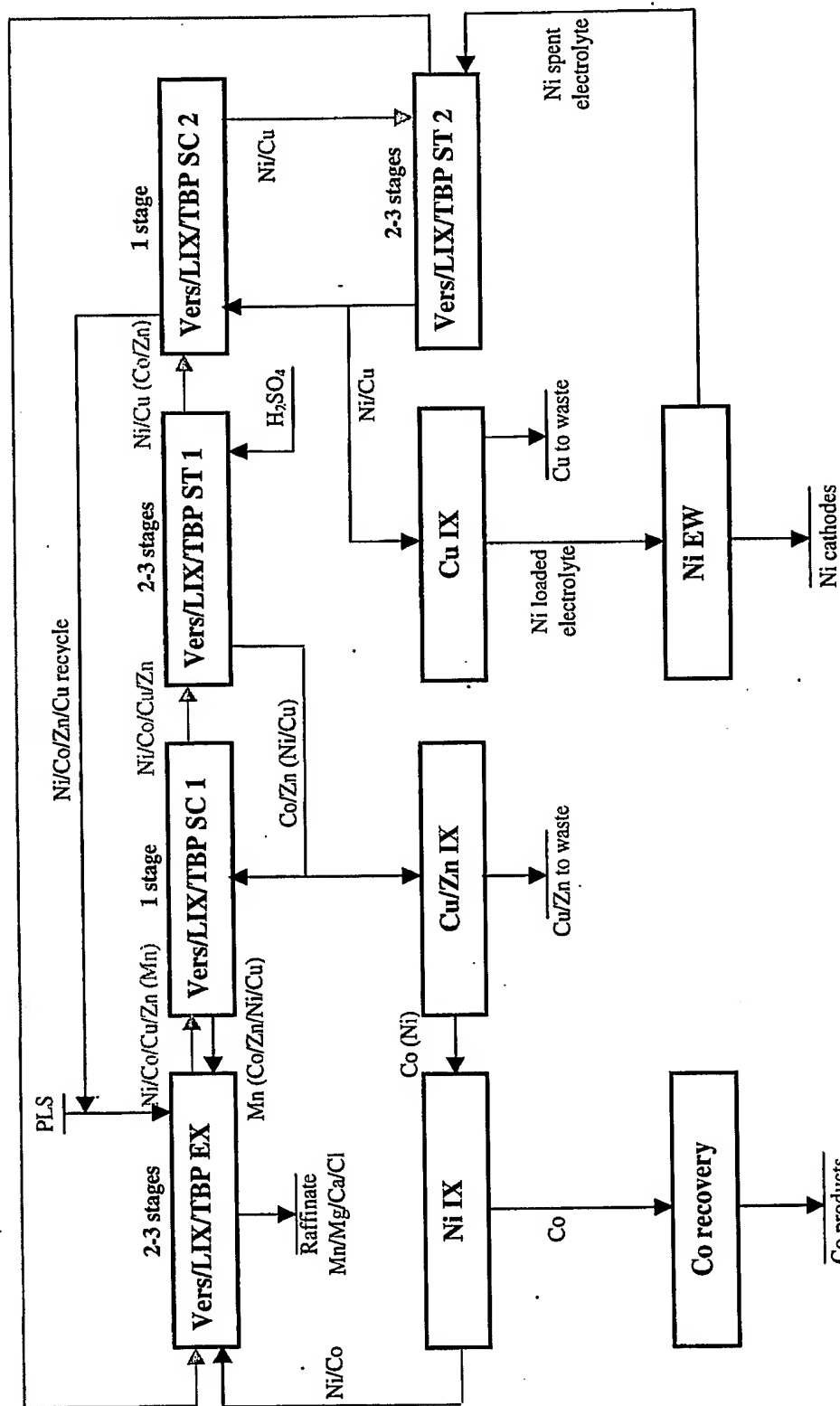


Figure 2

1. Minor elements in brackets



1. Minor elements in brackets

Figure 3

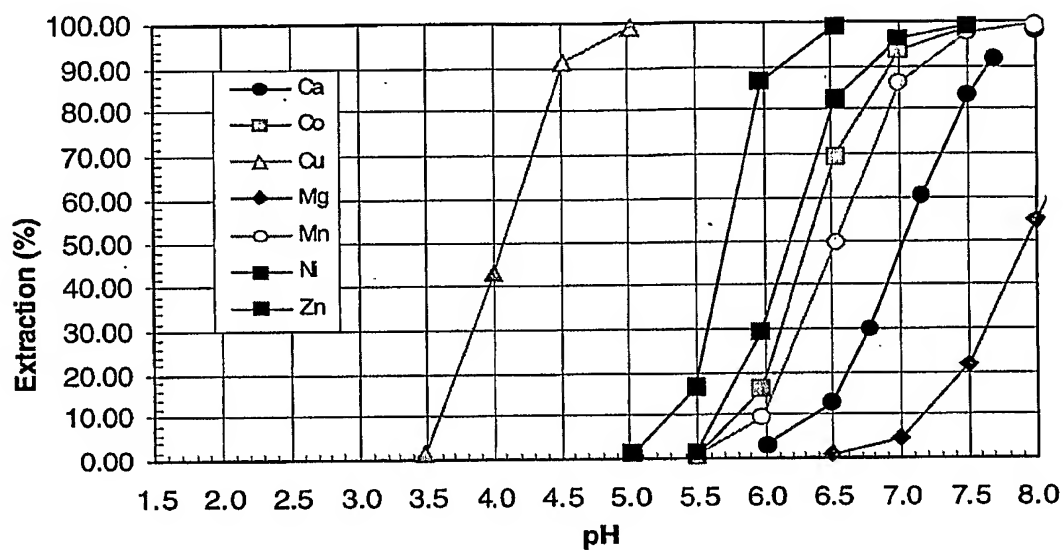


Figure 4

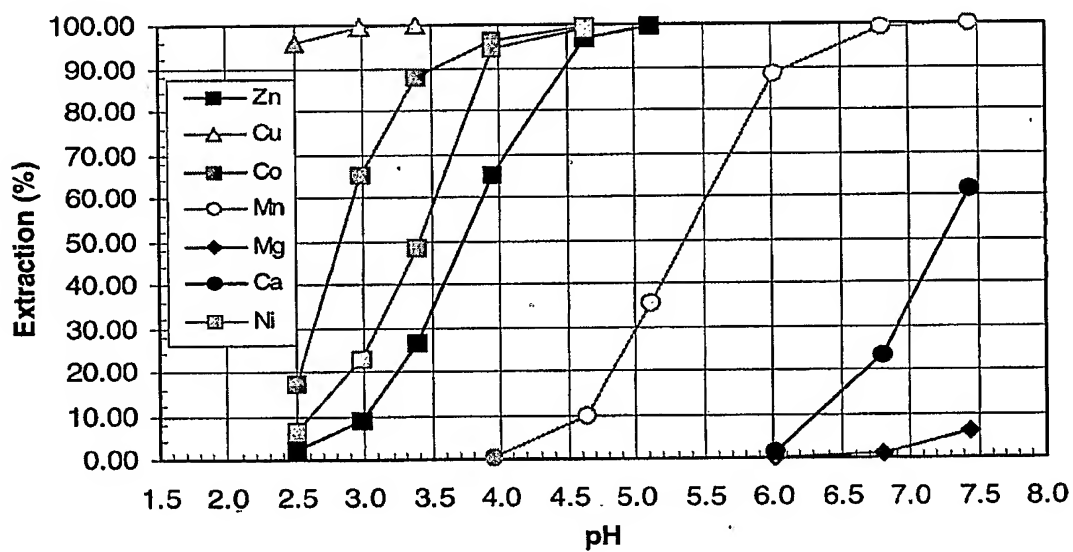


Figure 5

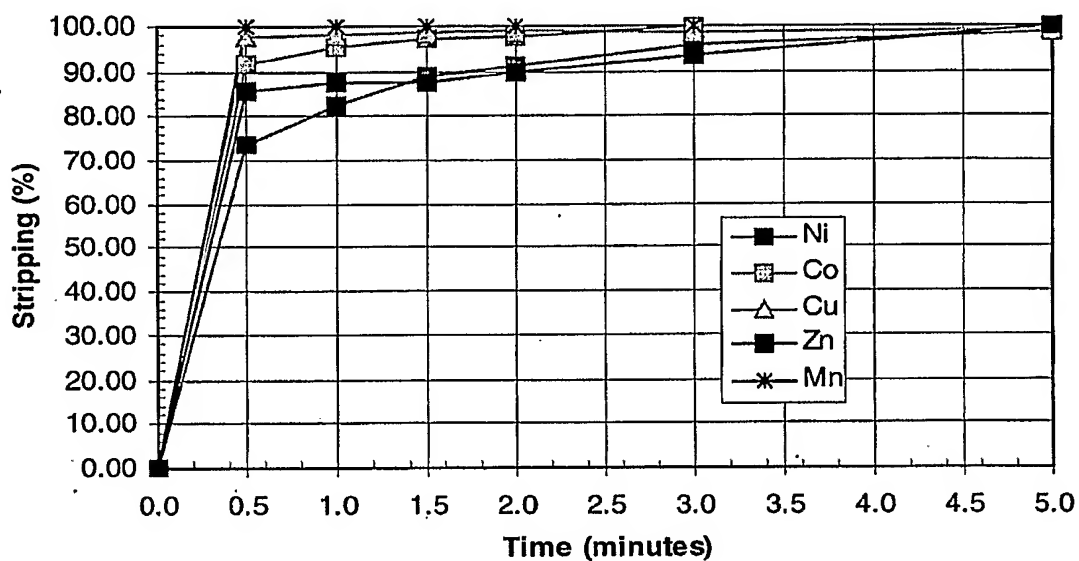


Figure 6

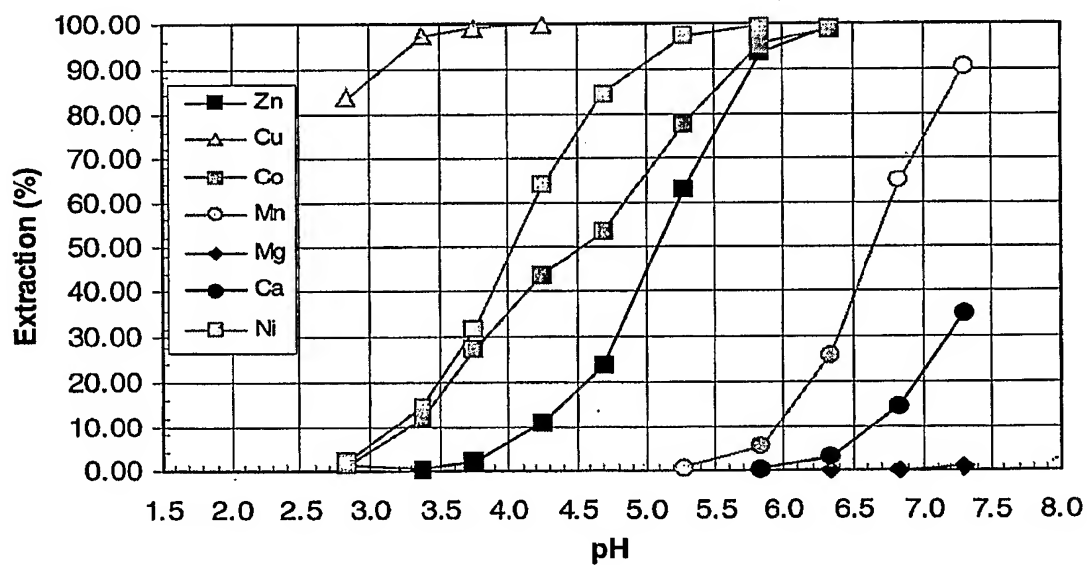


Figure 7



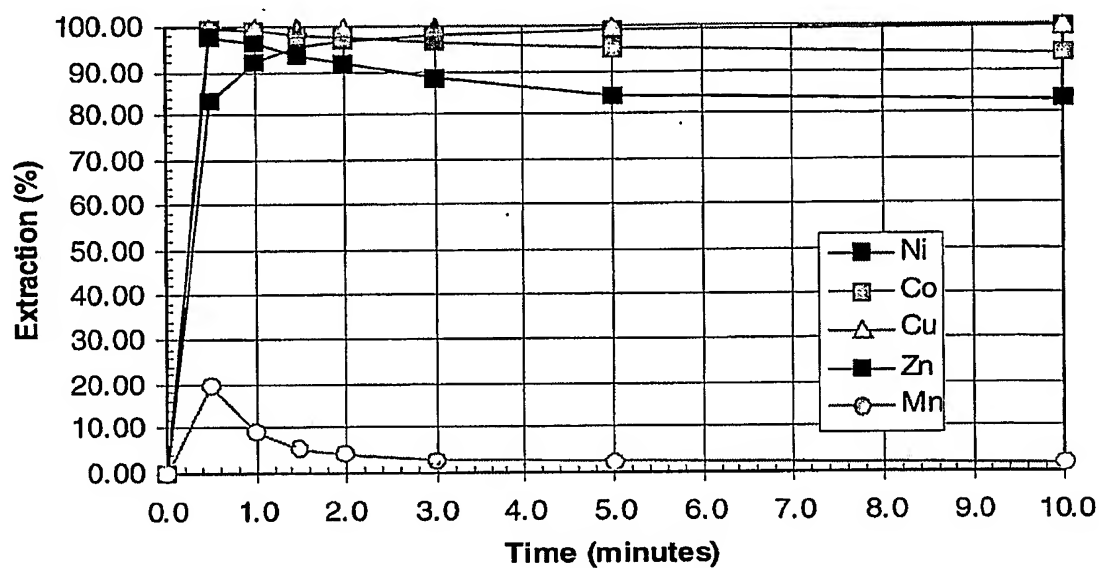


Figure 8

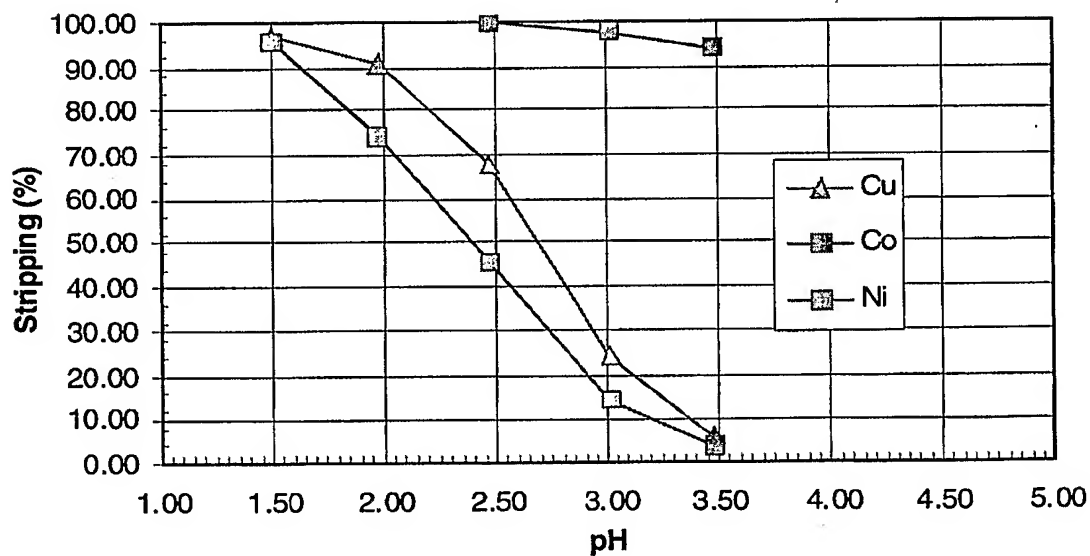
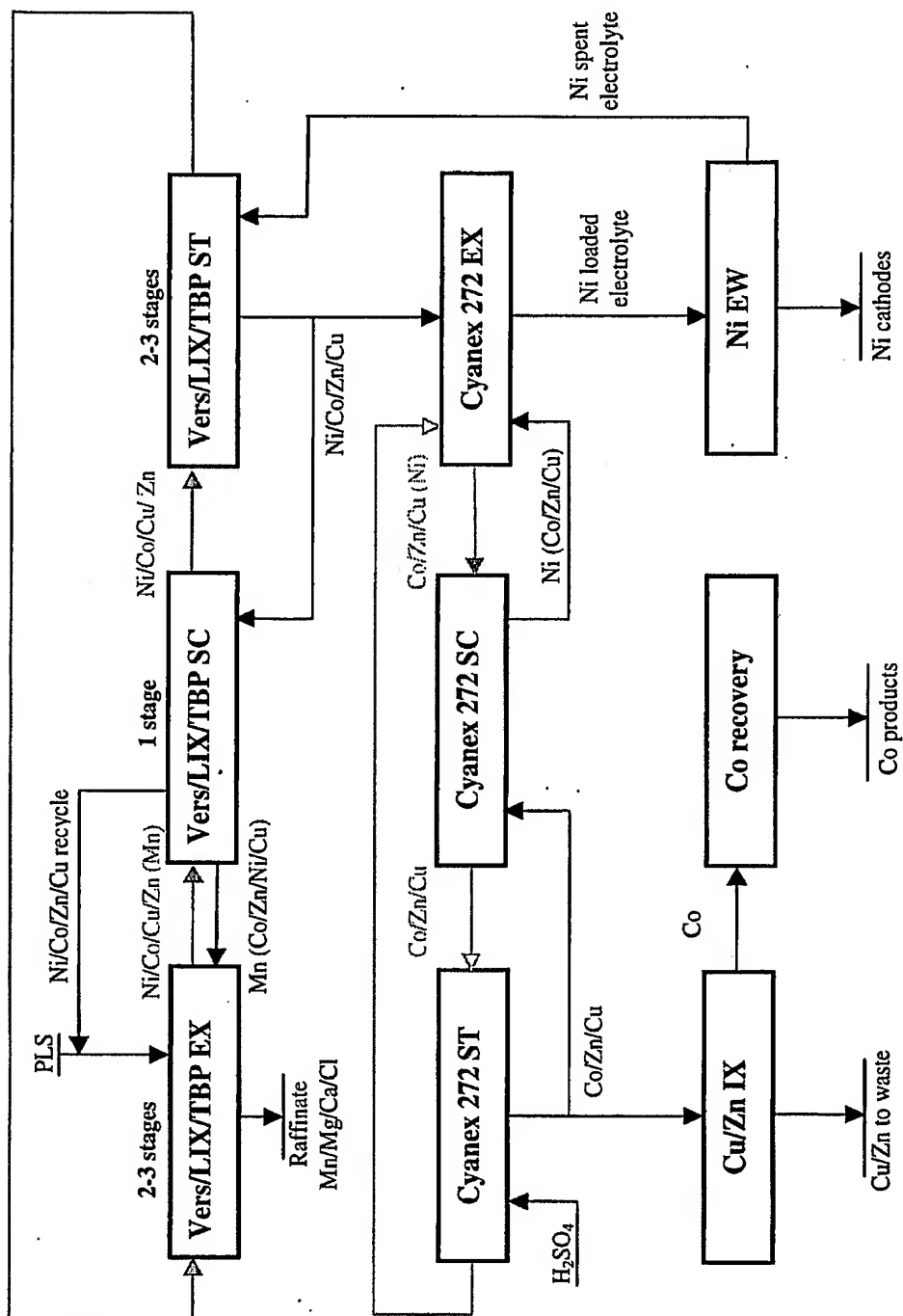


Figure 9



1. Minor elements in brackets

Figure 10